Deposition of In and Al doped ZnO thin films by spray pyrolysis technique and their characterization

A synopsis submitted

To

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- **INTRODUCTION**

Significant development has been occurred in the thin film deposition technology, since past few years. This deposition technology have several advantages over others such as large deposition area, high potential and cheaper in the cost. Thin film is a layer of substance or material, whose thickness is in the range of nanometers to few microns. These deposition techniques involve three basic phases [1]: first phase involve production of appropriate atomic molecular or ionic species, second transport of these species to substrate through a medium, and third condensation on the substrate either directly or via a chemical or electrochemical reaction to form a solid deposition. Thin films are deposited on the substrate to achieve better properties than that of bulk material offers. Films deposited on substrate are different from their bulk materials (grain and crystal size) may evident following effects.

1. Its hardness improves.

2. Its corrosion resistance increase.

3. Their magnetic saturation temperatures enhance.

4. Its electrical, optical and mechanical properties will enhance or change.

The semiconductor devices are a main application of the thin film deposition technology. Thin films of semiconducting oxide materials like TiO_2, ITO, Ga_2O_3 ZnO and SnO_2 have played important role for many optoelectronic devices and applications[2]. Among these zinc oxides (ZnO) thin films are semiconducting oxide films continue to receive a considerable amount of interest from both fundamental and application views, especially due to its following uncommon properties**.**

- It has high stability, and excitation binding energy (~60 meV).
- It is comparatively low cost, non toxic and highly durable in nature.
- It has a direct and wide band gap semiconductor (Eg~3.34eV at room temperature).
- It has high transparency over the complete visible range with a sharp cutoff at ~375nm.
- It has a high melting point (1975^{o}C) that suggests a strong bonding and implies that ZnO is thermal and chemical resistant material.

Undoped ZnO shows n-type conductivitybecause of the existence of constitutional defect. Its resistivity can be varied from semi insulating to semi metallic regime by selecting appropriate doping. However, doping creates disorder locations in the crystal structure.The performance

domain of ZnO can be significantly expanded by doping it with ions of different elements for example-

i. ZnO resistivity can be varied by doping it with group three elements such as gallinium (Ga), aluminum (Al) or indium (In) [3].
ii. Dilute magnetic semiconductor devices can be developed by doping ZnO with transition element such as cadmium (Cd), magnesium (Mg), manganese (Mn) and cobalt (Co) [4].
iii. P-type semiconductor materials can be produced by ZnO doped with various group VB elements such as nitrogen (N), phosphorus (P), arsenic (As) [5].
iv. To make optical devices, ZnO can be doped with optically active dopant such as rare earth elements [6].

- **LITERATURE REVIEW**

ZnO is a wide, direct band gap, n-type semiconducting material with many promising properties for blue/UV optoelectronics [7], transparent electronic devices [8], spintronic devices [9], antireflection coating [10], transparent electrode in solar cell [11], chemical and gas sensors applications [12].The literature study shows that the incorporation of group III ions enhances the optical and electrical properties of the ZnO.

- **Z. Shaban et al.** reported the deposition of ZnO thin film with three techniques, spray pyrolysis, spin coating and dip coating. The temperature and the height parameters were investigated to optimize the thin film deposition [13**]**.
- **E. Muchuweni et al.** reported Synthesis and characterization of ZnO thin films for the optoelectronic applications. A low resistivity of $6.03x10^{1}\Omega.cm$ were recorded which indicates the suitability of the ZnO micro-ring structured thin films for optoelectronic applications[14].
- **Suat Pat et al.** investigate effect of Al doping on the surface, optical, electrical and nanomechanical properties of ZnO thin film. The AFM results have been exhibit reduce of roughness values to the relatively low value of Al-doped ZnO. Al doping can affect the hardness of the ZnO. The hardness of the AZO film was calculated as 11 GPa [15].
- **Pankaj S. Kolhe et al.** describe the gas sensing performance of Al doped ZnO thin film for H_2S detection. The sensor response is found to be increased with the increase in doping concentration of Al [16].

- **F. Zahedi et al.** reported the effect of precursor concentration on structural, optical and electrical properties of ZnO thin films prepared by spray pyrolysis. He observed that the value of photocurrent and photoresponsivity are increased with increasing precursor concentration related to increase in grain size, porosity and quality of ZnO films[17].
- **R. Sankar Ganesh et al.** examined the gas sensing properties of Al-doped ZnO (6wt. %) thin films. The response of the Al-doped ZnO (6 wt. %) increased with increasing ammonia concentrations from 5 to 500 ppm [18].
- **S.P. Bharath et al.** studied the enhanced gas sensing properties of $In_xZn_{1-x}O$ thin films prepared by spray pyrolysis method. $In_{0.03}Zn_{0.97}O$ thin films showed good sensitivity towards ethanol, with sensitivity of 30% towards 25ppm of ethanol [19].
- **Haiping He et al.** report an unusual violet emission centered at 3.1 eV from indium doped ZnO nanowires. The violet emission can be observed only below 180K and shows thermal quenching with unexpectedly small activation energy of nearly 36 meV [20].
- **K. W. Liu et al.** report the optical and magnetic properties of ZnO, $Zn_{0.97}In_{0.03}O$, and $Zn_{0.94}In_{0.06}O$ nanowires. He observed that In doped ZnO is a viable approach to realizing high-quality optical properties and RTFM, which may help to advance optoelectronic and spintronic devices [21].
- **S. Alamdari et al.** reported synthesis of Al and In co-doped ZnO (AIZO) nanoparticle by the sol gel route. He found that prepared AIZO composite also exhibited strong emission peaks in the yellow-orange range at room temperature. Results showed that AIZO nanoparticles could be good candidate for the use in lighting applications [22].

- **OBJECTIVE OF RESEARCH**

Following are the objectives of our research work:

1. Deposition of **In and Al doped ZnO** thin film by chemical spray pyrolysistechnique.
2. Investigation on the structural, morphology, optical, photoluminescence and gas sensing properties of ZnO thin films.
3. To study the effect of **In and Al** doping on morphological, optical, photoluminescence and gas sensing properties of ZnO thin films.

- **HYPOTHESIS OF RESEARCH**
  - The research work is directed to obtain new and improved **In and Al doped ZnO** thin films.
  - The physical and optical properties of the films will be affected by the metal doping.
  - The effect of doping depends on the factors such as concentration.So it is expected to grow the crystal by varying the concentration and to report to grow the films.
  - The gas sensing properties of the films will impact by the doping materials.

- **METHODOLOGY**
  - **Fabrication of Thin Films:**

    It is proposed to grow **In and Al doped ZnO** thin films by chemical Methods (Spray Pyrolysis/ Chemical Bath Deposition). At initial stages the efforts will be done in order to fabricate **ZnO** thin films on glass substrates. In the next stage **In doped ZnO** and **Al doped ZnO** thin films will be fabricate.
  - **Characterizations of Fabricated thin films:**

1) **Structural Analysis:** The X-ray analysis technique will use to know the information about interplaner distance (d), crystal structure of the **In and Al doped ZnO** films. Also from the XRD data; the crystal parameters such as lattice parameters (**a** and **c)**, c/a ratio, volume of unit cell (v), average crystalline size of particle etc will be calculate.
2) **Morphological Studies:** SEM or TEM techniques will be utilized to reveal morphological surface features of **In and Al doped ZnO** films.
3) **Compositional studies:** The film composition will be study with the EDS or EDAX techniques and correlation will be made with as taken and observed contents.
4) **Optical Studies:** The absorbance/transmittance, absorption coefficient (α), energy band gap (E_g), refractive index etc. will be study by using UV-VIS spectrophotometer.
5) **Photoluminescence Studies:** Photoluminescence properties of **In and Al doped ZnO** films will be studied.
6) **Gas sensing Studies:** Gas sensing properties of the **In and Al doped ZnO** films will be studied.

- **IMPORTANCE OF STUDY**

- Zinc Oxide (ZnO) has high electrical resistivity, but this disadvantage can be reduced by the doping ZnO with group III ions (B^{3+}, Al^{3+}, Ga^{3+}, and In^{3+}). These ions ensure extra electrons and improve optical, electrical, thermal, and magnetic properties of undoped ZnO.
- Indium (In) is a group III element which can be considered as most efficient dopant in ZnO to enhance its optical and photoluminescence properties. When indium (In^{+3}) substituted on ZnO then loosely bound extra electron of indium occupies the conduction band and act as a carrier in ZnO matrix.
- Aluminum (Al) most preferred dopant element due to its difference in ionic radius and low cost material. The substitution of Zn^{2+} ions with Al^{3+} in ZnO lattice causes that the increase of electrical conductivity due to the increase of charge carriers. This situation is suitable for fabrication of transparent electrodes in solar cells, gas sensors and also for ultrasonic oscillators
- Recently, ZnO is one of the most promising materials for gas sensing application. The cost-effective large-scale production of these films and the development of ZnO films with improved properties are key challenges in the field of production in gas sensors.

- **PROPOSED WORK PLAN**

Year – wise plan of work and targets to achieve.

- **Year I – Plan:**

A thorough literature survey and collection will be done in order to get more information about work already done and scope of present work. The literature includes collection of Journals, Books and some research papers related to the research work will be completed. Various chemicals (high purity) will be procured and efforts will be made to deposit good quality **Pure and doped ZnO** films.

- **Year II – Plan:**

In this year, all preparative parameters will be optimized in order to get good quality thin films of **In and Al doped ZnO**on glass substrates. The structural, optical and photoluminescence properties of fabricate film will be studied by using XRD, SEM or TEM, UV-VIS spectrophotometer and PL spectrum measurement system.

- **Year III – Plan:**

In the last year, the gas sensing properties of the**In and Al doped ZnO** thin films will be study. To collect all data and analyze the result to publish research papers in reputed national and international journals. To submit the final thesis of the proposed work for doctoral degree.

- **CHAPTER SCHEME**

Chapter 1: Introduction

Chapter 2: Literature Review

Chapter 3: Materials And Methods

Chapter 4: Result and discussion

Chapter 5: Conclusion and future scope

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